2013 Hydrogen and Fuel Cells Program
Annual Merit Review and Peer Evaluation Meeting
Arlington, Virginia – May 13-17, 2013

Non-Precious Metal Fuel Cell Cathodes: Catalyst Development and Electrode Structure Design

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Los Alamos, New Mexico 87545

Project ID: FC107

Overview

Timeline

- **Start date:** April 1, 2013
- **End date:** Three-year duration
- **Completion:** 0% (new project)

Budget

- **Total funding estimate:**
  - DOE share: 3,998 K
  - Contractor share: 1,008 K
- **FY13 funding received:** 155 K

Barriers

- **A. Activity** (catalyst; MEA)
- **B. Durability** (catalyst; MEA)
- **C. Power density** (MEA)

Partners – Principal Investigators

General Motors
– Joseph Ziegelbauer

IRD Fuel Cells
– Madeleine Odgaard

Carnegie Mellon University
– Shawn Litster

University of Rochester
– Michael Neidig

University of Waterloo
– Zhongwei Chen

Oak Ridge National Laboratory
– Karren More

Objective

Advance non-PGM cathode technology through the development and implementation of novel materials and concepts for cathode catalysts and catalytic layers with (i) oxygen reduction reaction (ORR) activity viable for practical fuel cell systems; (ii) much improved durability; (iii) sufficient ionic/electronic conductivity within the catalyst layer; (iv) adequate oxygen mass transport; and (v) effective removal of the product water.

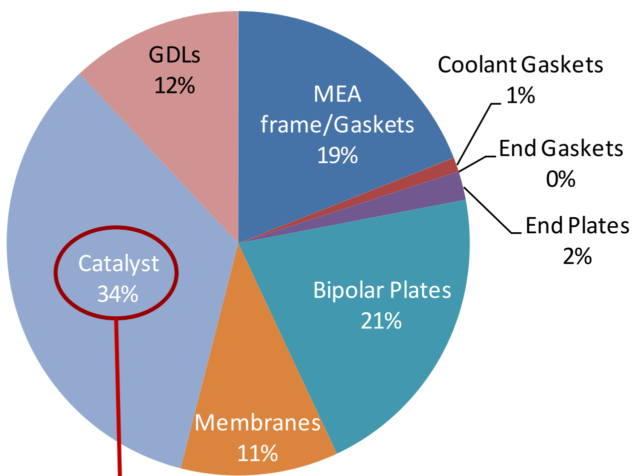
Table 3.4.13 Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Unit	2011 Status	Targets	
			2017	2020
Non-Pt catalyst activity per volume of supported catalyst	A / cm^3 @ 800 $mV_{IR\text{-}free}$	60 (measured at 0.8 V) 165 (extrapolated from >0.85 V)	300	300

Technical Targets

- **Volumetric catalyst activity in MEA at 0.80 V (*iR*-free), 80°C:** $\geq$ 300 A cm^{-3}
- **Four-electron selectivity (RRDE):** $\geq$ 99% (H_2O_2 yield $\leq$ 1%)
- **MEA maximum power density at 80°C:** $\geq$ 1.0 W cm^{-2}
- **Performance loss at 0.80 A cm^{-2} after 30,000 cycles in N_2:** $\leq$ 30 mV

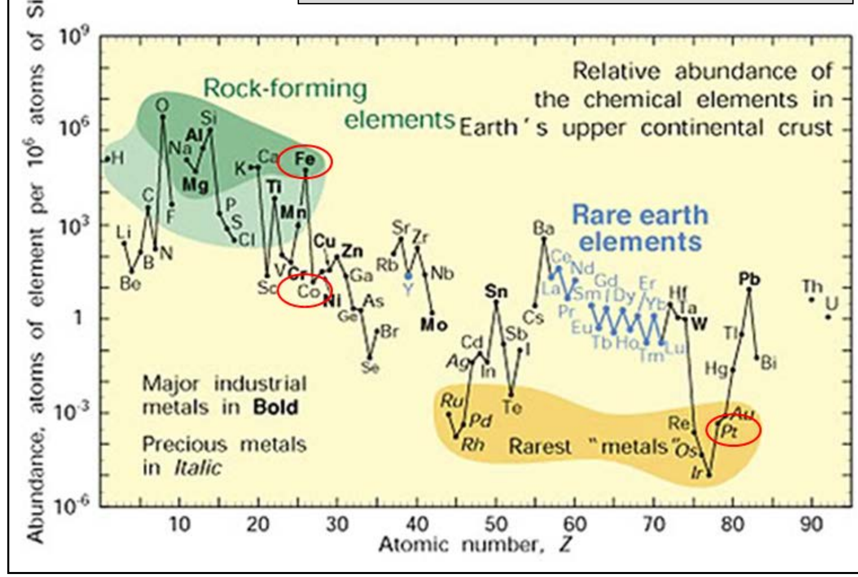
Fuel Cell Cost Breakdown
(at Pt price of $1,100/oz)

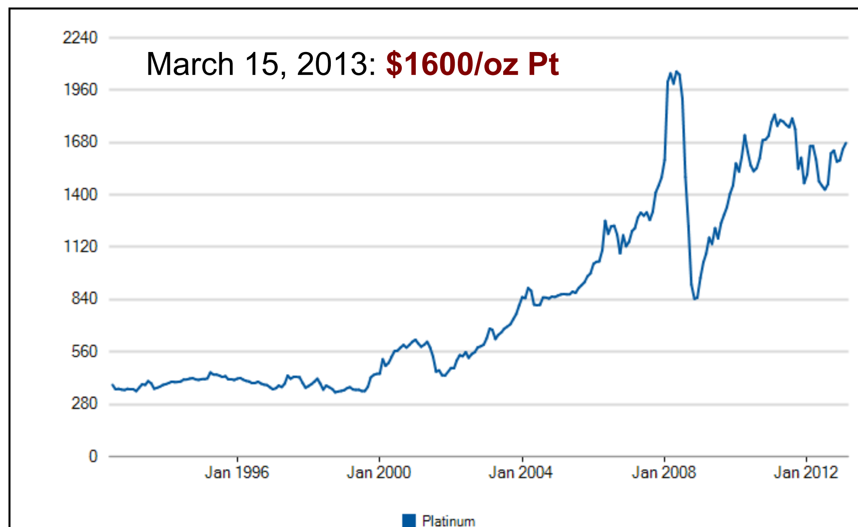


ca. **43%** at ~$1,600/oz today

James *et al.,* DTI, Inc., 2010 DOE Hydrogen Program Review, Washington, DC, June 9, 2010

Frédéric Jaouen, LANL Presentation, April 2012





http://www.platinum.matthey.com/prices/price-charts

Approach: Project Overview

ORR Catalyst Development

- Multiple nitrogen precursors and alternative supports (LANL)
- Non-pyrolyzed phthalocyanine-derived catalysts (Waterloo)
- Nitrogen-doped carbon nanostructures (LANL, Waterloo)

Characterization & Active-Site Determination

- Advanced catalyst characterization (LANL, Waterloo, GM, ORNL)
- Active-site determination using oxygen analogs as surface-specific probes (UR, LANL)

Electrode Design, Integration & Optimization

- GM model validation and parameter estimation using in-situ microstructured electrode scaffold measurements (GM, CMU)
- Microstructually-consistent models (ORNL, CMU)
- Electrode optimization (CMU, GM, LANL, Waterloo)

MEA Fabrication, Optimization & Scale-up; Deliverable

- MEA fabrication, optimization and scale-up (IRD, GM, LANL)
- Project deliverable: 50 cm^2 or larger MEAs (GM, IRD)

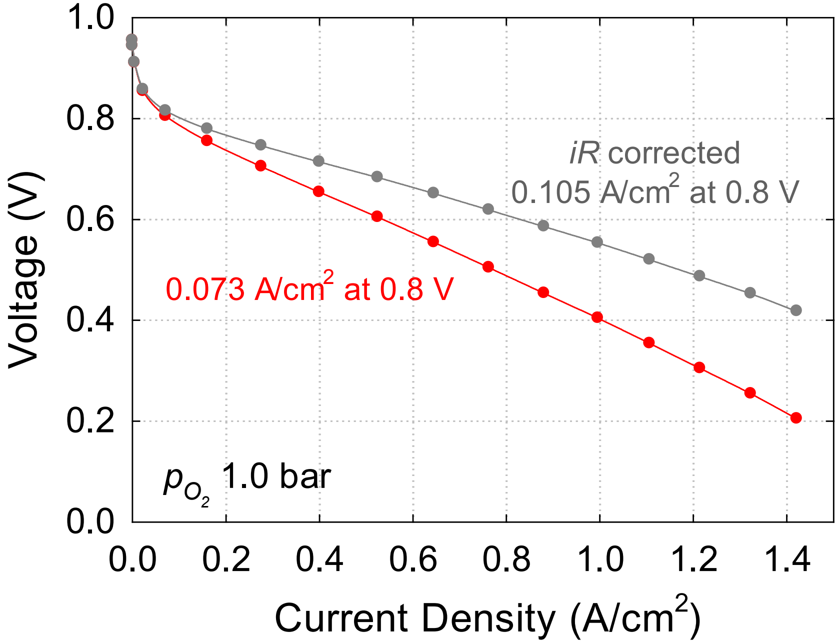
Approach: FY13 & FY14 Milestones

Date	Milestones
September 2013	Project management: Execute all 5 subcontracts.
March 2014	Electrode design: Image 3D structure of a state-of-the-art LANL electrode by Nano-XRT and compute effective transport properties.
April 2014	Active site determination: Validate surface-probe approach for a non-PGM catalyst using at least two characterization techniques.
May 2014	Heat-treated catalysts: Synthesize nanotube-based and graphene-based metal-free ORR catalysts; demonstrate $E_{½} \geq 0.60$ V *vs.* RHE.
August 2014	Electrode design: Perform MES measurements of the electrolyte potential distribution in cathodes with two leading FY14 material sets and use data to evaluate predictive capabilities of existing GM and CMU models.
September 2014	Heat-treated catalysts: Demonstrate $i_{0.8V} \geq 150$ A cm^{-3}, $\eta > 95\%$, and 30,000-cycle performance loss of no more than 50 mV ($\Delta E_{½}$ and/or ΔV at 0.8 A cm^{-2}).

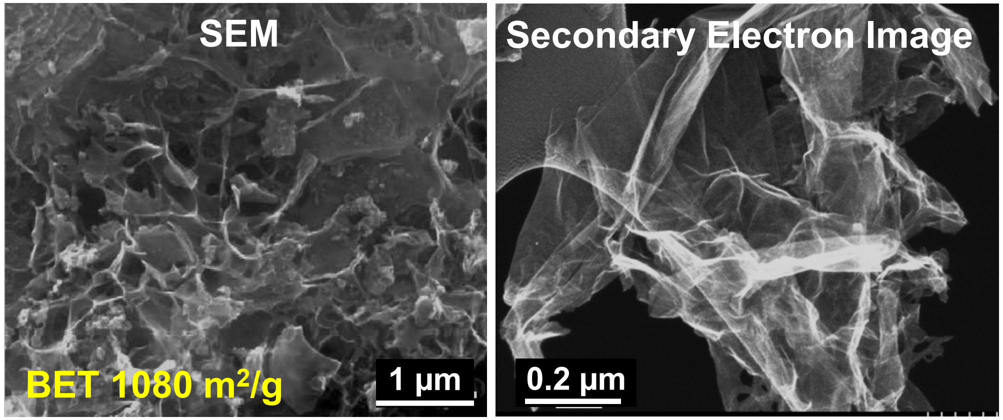
***Note:* This is a new project; information that follows reflects state of the art and research to be performed**

Catalyst Development: High Surface-Area Polyaniline-Iron Catalysts

Anode: 2.0 mg cm^{-2} Pt; **Cathode:** 4.1 mg cm^{-2} **Cell:** 80°C; 100% RH, **Membrane**: Two Nafion® 212's



Morphology

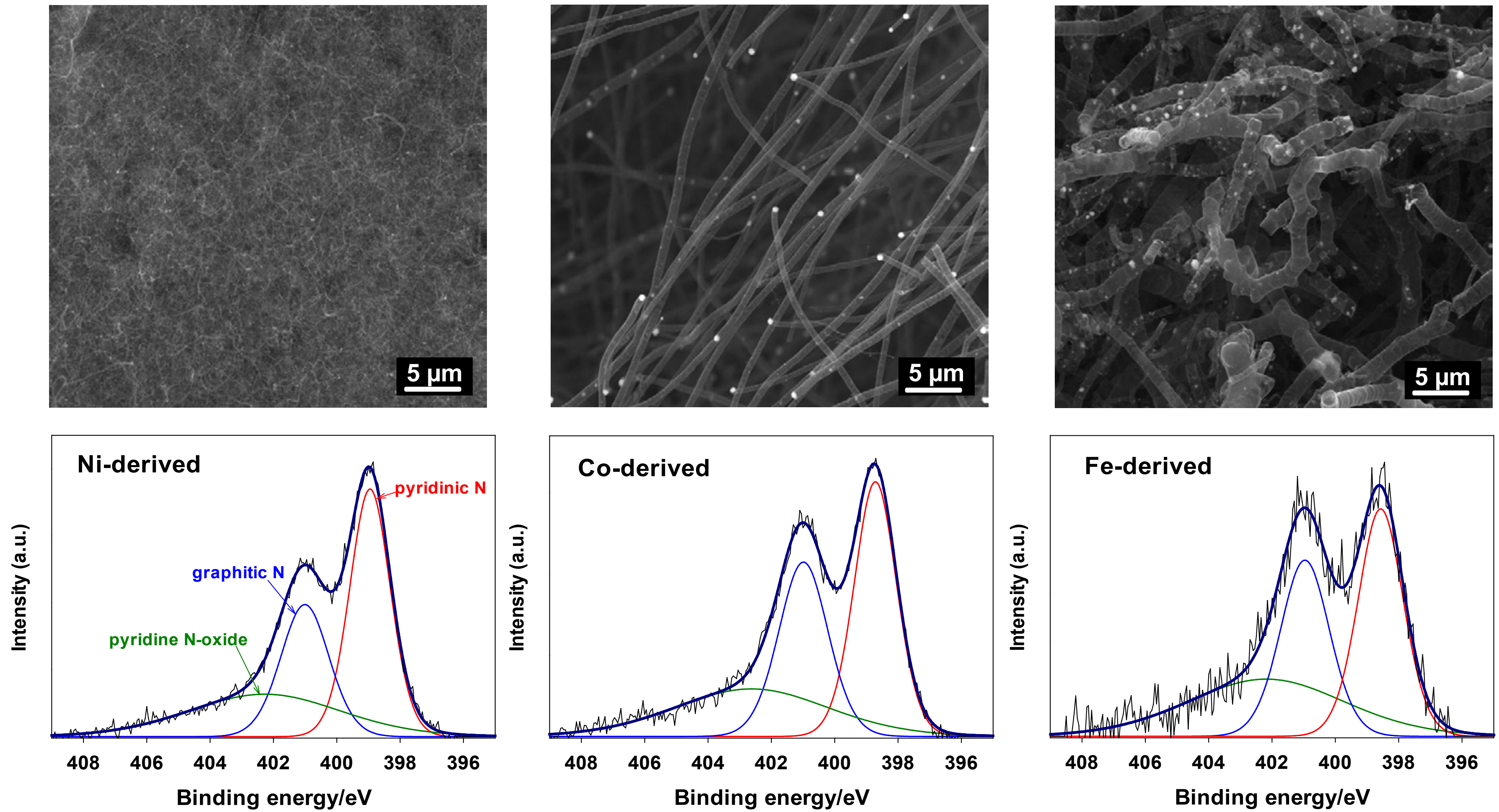


Elemental Analysis

S	N	C	Fe	O
0.3	3.6	89.7	0.2	6.2

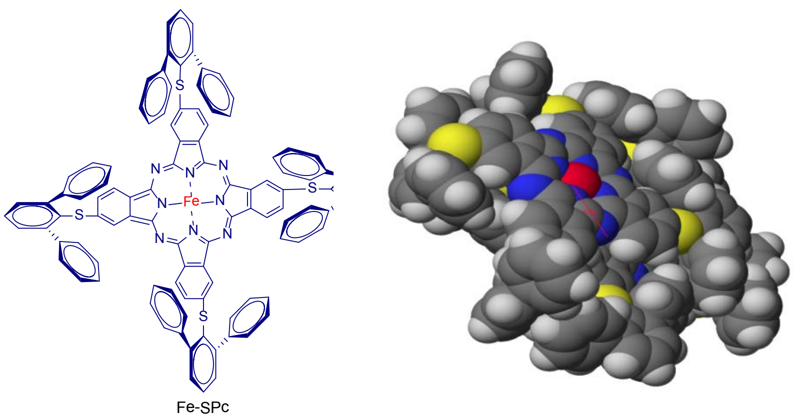
- **Polyaniline-derived catalyst yielding ORR current density close to 0.1 A/cm² at 0.8 V in fuel cell testing**
- **High-surface-area graphene-rich porous morphology likely acting as a host for active ORR sites**

Catalyst Development: Nitrogen-Functionalized CNTs

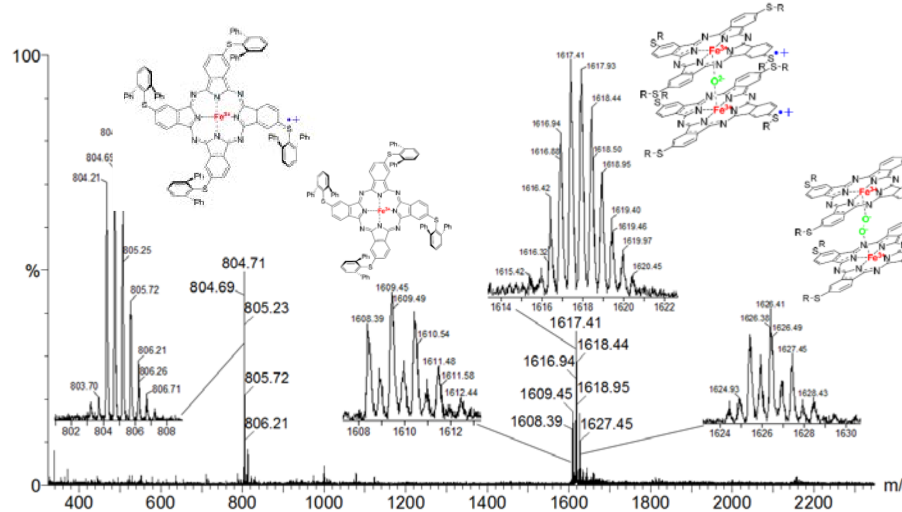


- **Carbon tubes synthesized in one step with high yield; no further purification needed**
- **Tube diameter and nitrogen functionalities depending on the transition metal used**
- **Various combinations of transition metal yielding CNTs with desired properties**

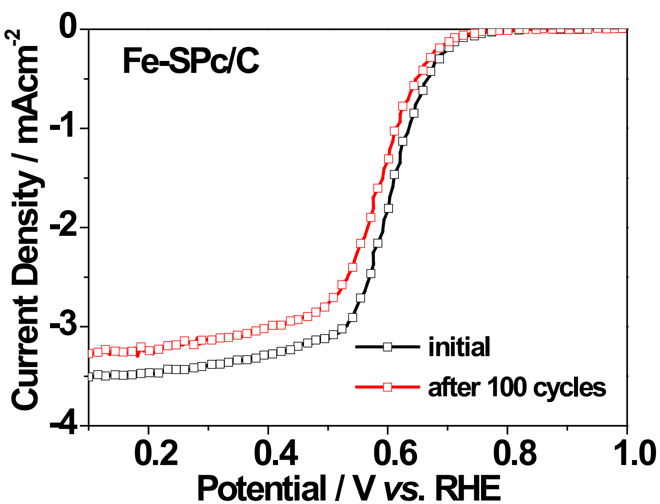
Catalyst Development: Non-Pyrolyzed Phthalocyanine-Derived ORR Catalysts



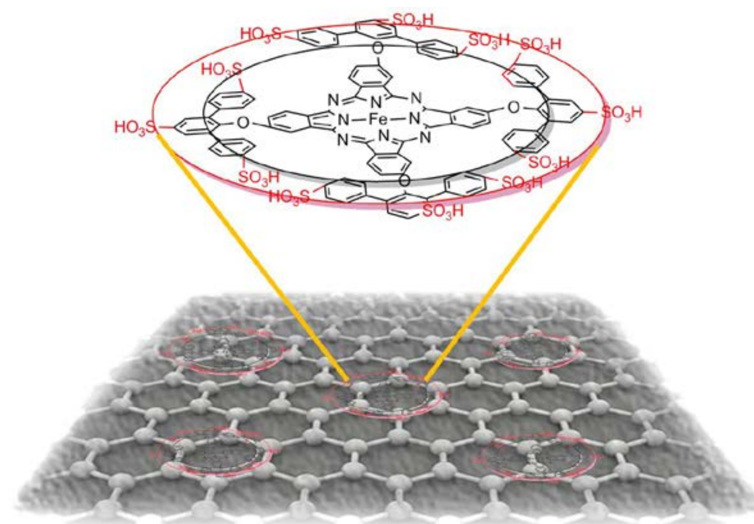
Space-filling stacking model of Fe-(Sulfur)Pc



Electrospray spectrum of Fe-SPc



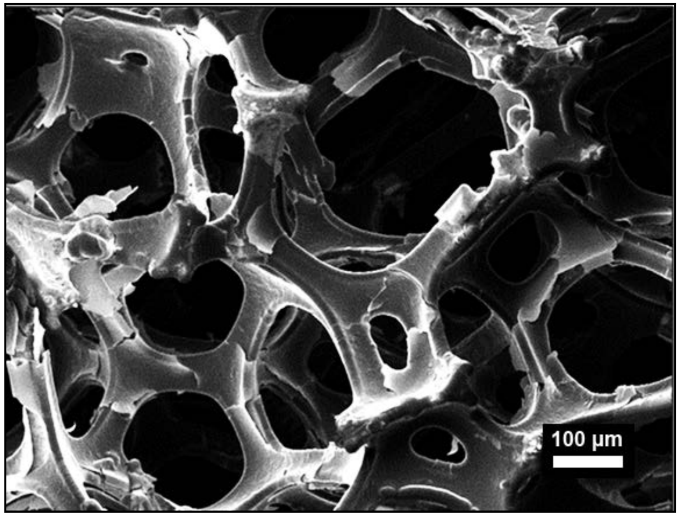
RDE: 0.1 M $HClO_4$, 5 mV s^{-1}, 25°C
(cycling: N_2, 0-1.2 V, 50 mV/s)

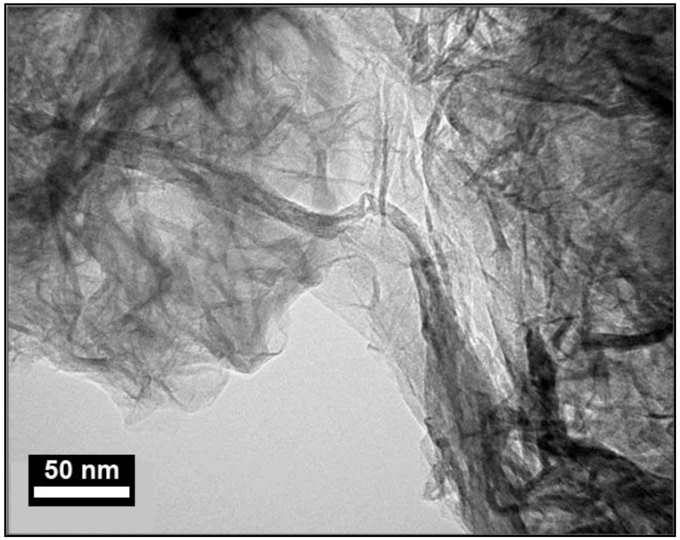


Graphene-supported Fe-SPc catalysts (Future work)

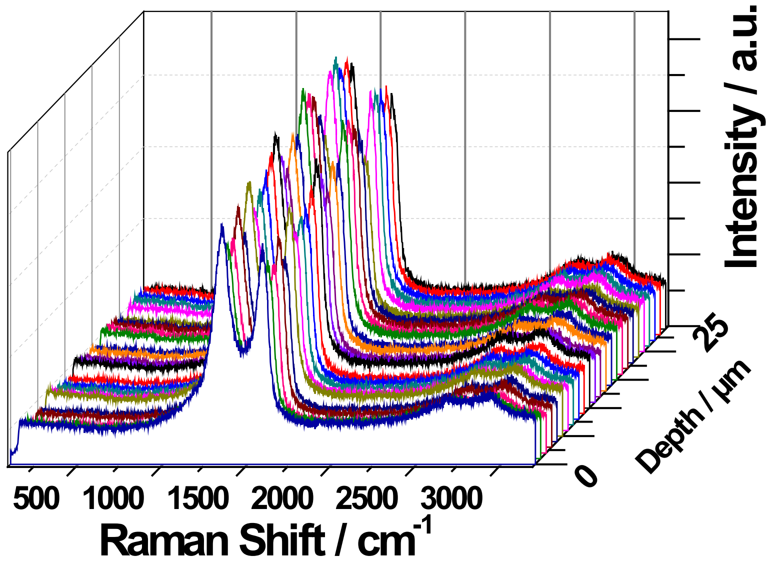
Catalyst Development: Graphene-Based Metal-Free 3D Structures

3D Graphene-Foam Electrodes





Raman Mapping of Electrode

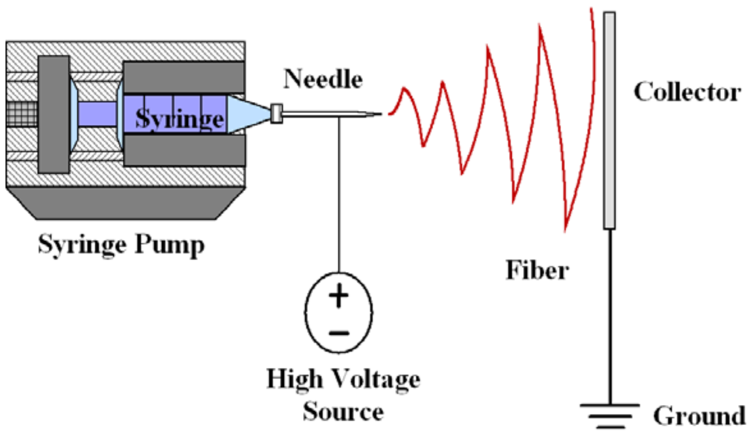


- 3D graphene-based structures promising high catalyst utilization without giving away good electron conductivity
- Methodology possibly adaptable to heat-treated non-precious metal ORR catalysts under development at LANL

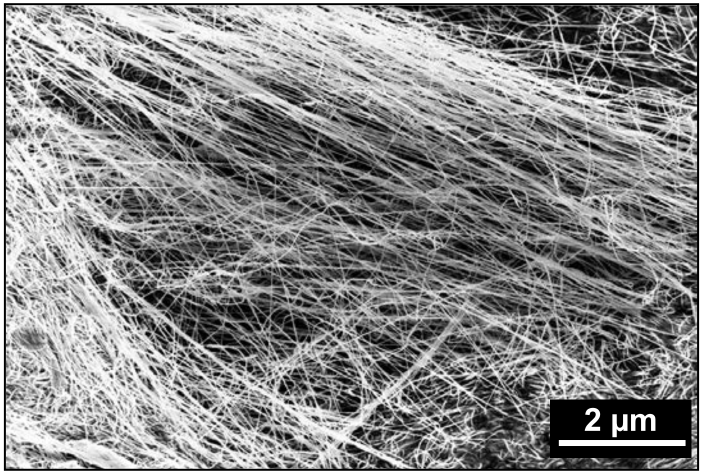
Materials synthesis in progress;
ORR performance to be evaluated soon.

Catalyst Development: Electrospun Catalysts and 3D Electrodes

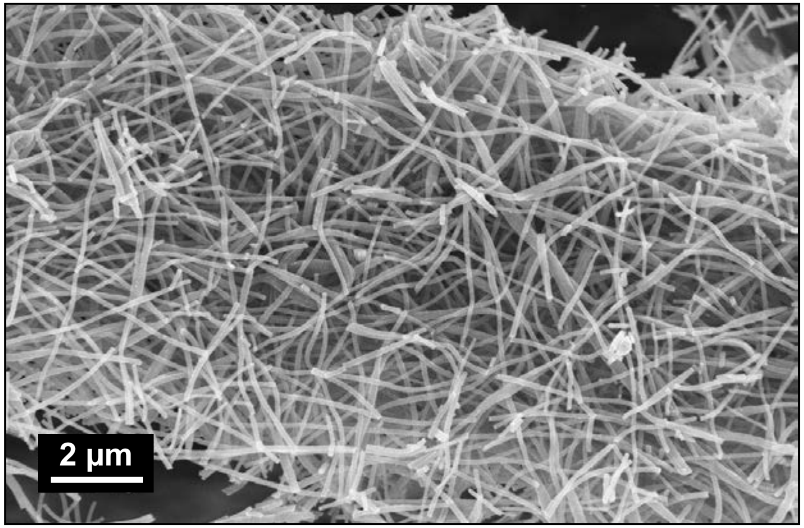
Principle of Electrospinning



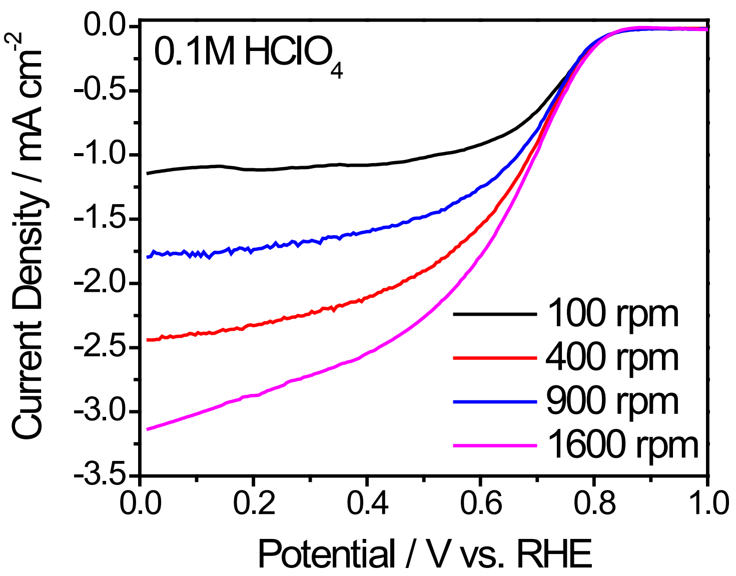
Polyacrylonitrile (PAN) Nanofibers



Heat-Treated Fe-PAN Nanofiber Catalyst

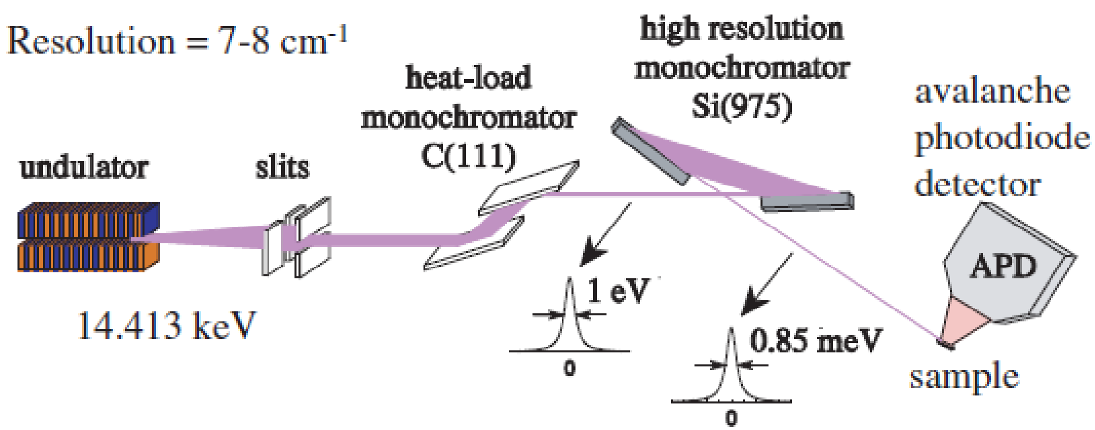


RDE: 0.1 M $HClO_4$, 10 mV s^{-1}, 25°C



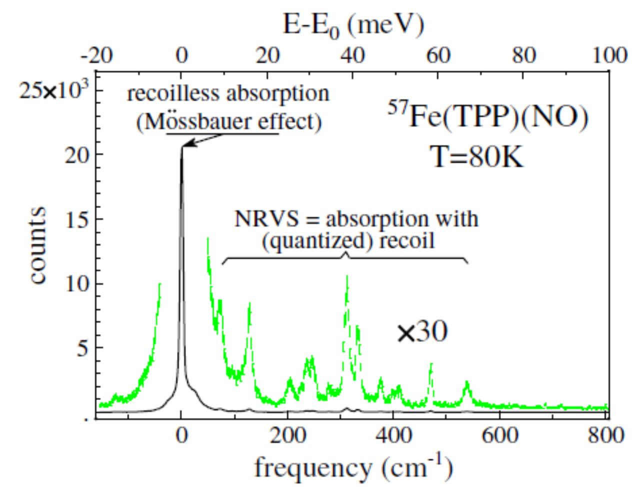
Catalyst Characterization: NO as a Molecular Probe; NRVS

- **Nitric oxide, $NO_{(g)}$, an O_2-analog forming stable, non-reactive complexes with Fe used to study O_2 binding to Fe sites in metalloenzymes**
- **When combined with Fe-specific spectroscopic methods, the O_2-analog approach provides**
  - ✓ insight into the electronic/geometric structure of O_2-binding Fe site
  - ✓ mechanism of O_2 activation/reduction (when combined with DFT methods)
- **Nuclear Resonance Vibrational Spectroscopy (NRVS) – an ideal technique for studying surface iron probed by $NO_{(g)}$**
  - ✓ Vibrational technique capable of providing complete set of bands corresponding to the motion of Mößbauer-active nuclei, i.e., ^{57}Fe
  - ✓ Combines nuclear excitation (classical Mößbauer effect) and molecular vibrations
  - ✓ Ultimate selectivity: Only vibrational modes of the probe ^{57}Fe nucleus contribute to the signal
  - ✓ Not subject to the selection rules of optical methods (e.g., Raman) → complete vibrational spectrum, including Fe-ligand vibrations



Sector 3 at Argonne National Laboratory

Scheidt *et al., J. Inorg. Biochem.* **99**, 60, 2005



NRVS of $^{57}Fe(TPP)$

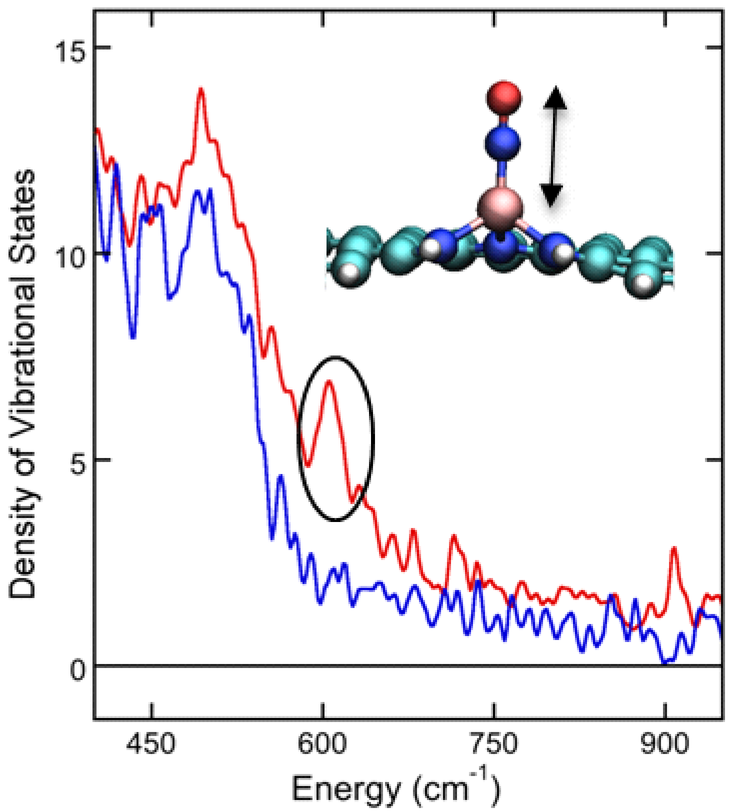
Scheidt *et al., J. Inorg. Biochem.* **99**, 60, 2005

Catalyst Characterization: NRVS and DFT Spectral Simulation

- Perturbation of some fraction of Fe sites found to occur upon $NO_{(g)}$ treatment
- Fe vibrational changes observed in both the low energy region (< 400 cm^{-1}) and in the higher energy region (> 500 cm^{-1})

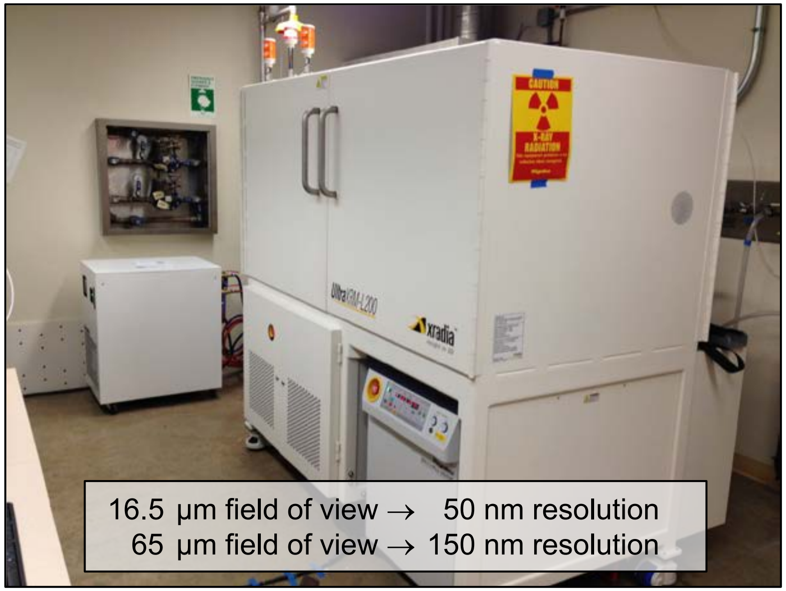
Surface Fe found to be present in PANI-Fe-C ORR electrocatalyst

NRVS: Electrochemically reduced (blue) and reduced plus NO-treated (red) PANI-Fe-C catalyst

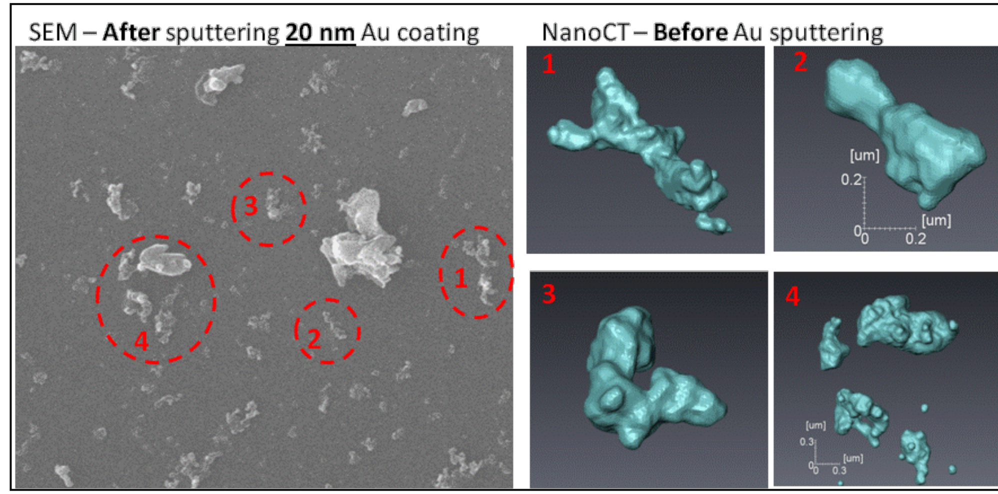


- **Most distinct NRVS peak at ~ 606 cm^{-1} (circled)**
- **3N-coordinated Fe above C monovacancy yielding DFT Fe-NO bond stretch of ~ 608 cm^{-1} (consistent with NRVS); Fe ~1.1 Å above the C plane with no ligand and by ~1.2 Å with O_2 attached)**
- **Fe-NO bond stretch frequency from DFT for the bi-nuclear (5N-2Fe) site giving ~ 617 cm^{-1} (consistent with NRVS within experimental error)**
- **4N-coordinated Fe in C bivacancy yielding DFT Fe-No bond stretch of ~ 690 cm^{-1} (poor agreement with NRVS)**

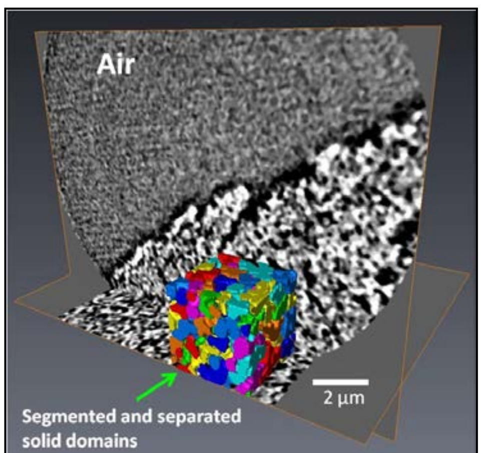
Electrode Design: Nanoscale X-Ray Computer Tomography Imaging



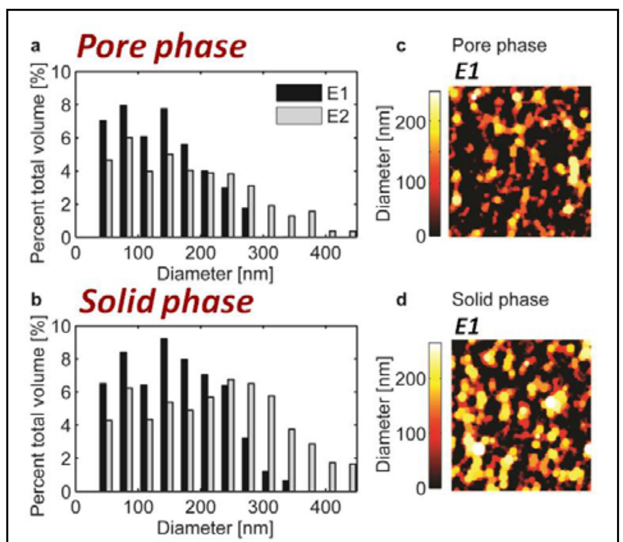
Simultaneous 3D Imaging of Many Dispersed Catalyst Aggregates from Ink



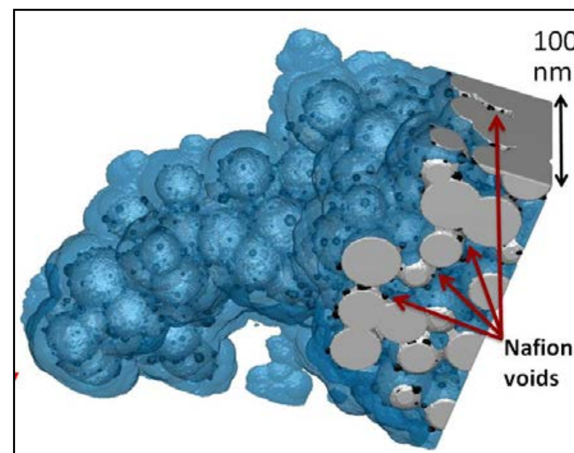
Electrode Structure



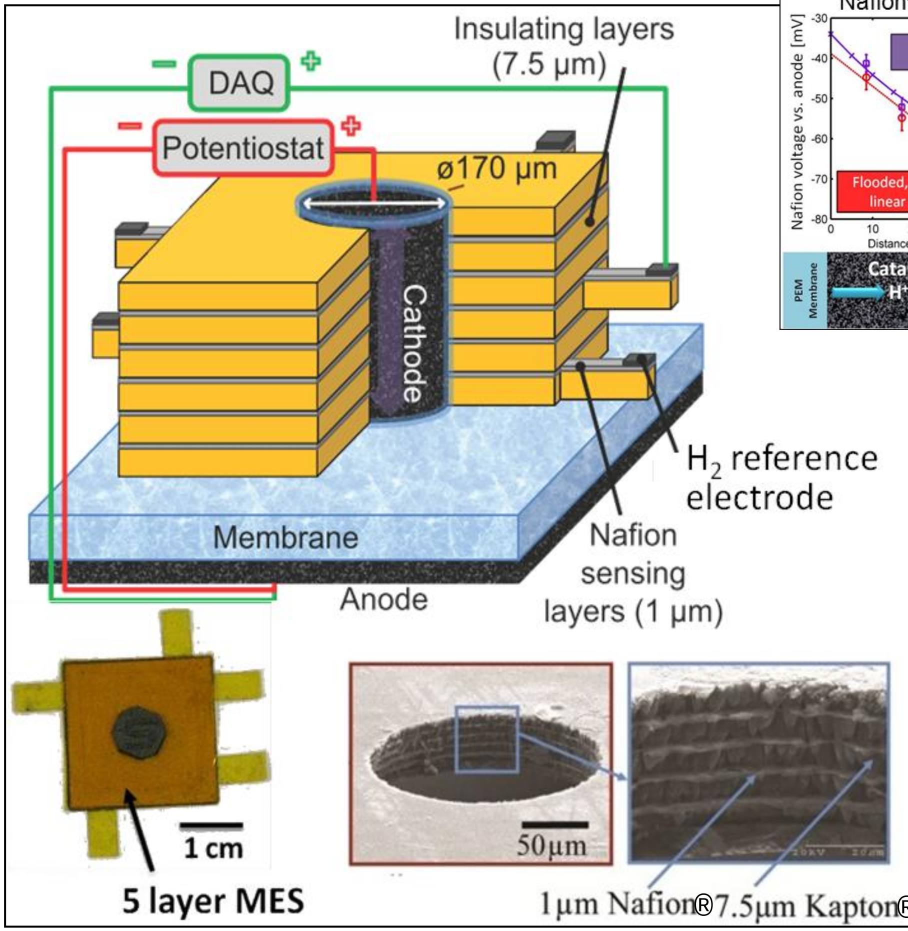
Morphology Statistics

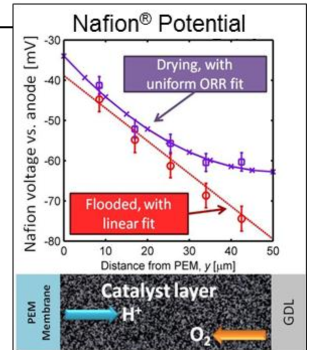


Particle-Scale Reconstruction

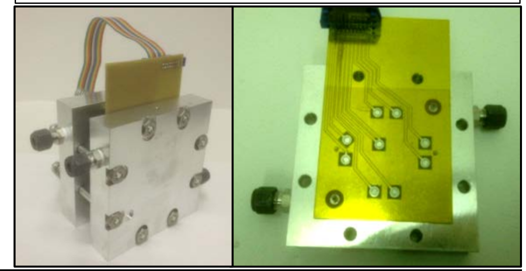


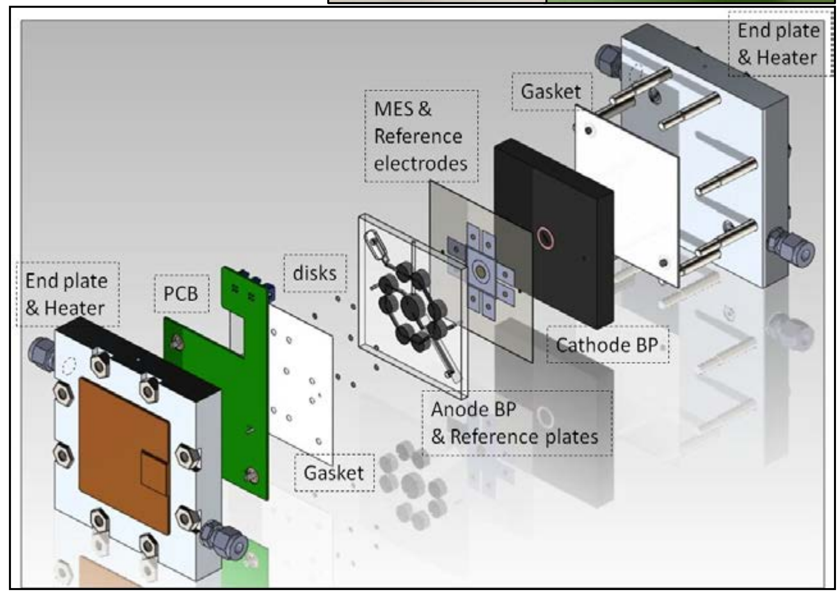
Electrode Design: Microstructured Electrode Scaffold (MES) Diagnostics





New MES Hardware
PCB Plate & Internal Manifolds

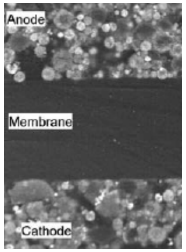




- **Micro-sensor array for measuring spatiotemporal, through-plane distribution of potential, conductivity, and reaction rate**
- **Ultramicroelectrode measurements of O_2 concentration by flux interrupt method**
- **New hardware for improved measurements with resolution approaching 2 µm**
- **New *in situ* current-probe technique for conductivity determination**

MEA Fabrication: Targets and MEA Fabrication Approach

Electrode design

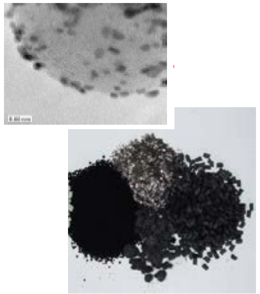


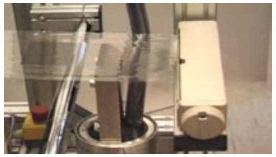
MEA Fabrication

Target MEA Performance

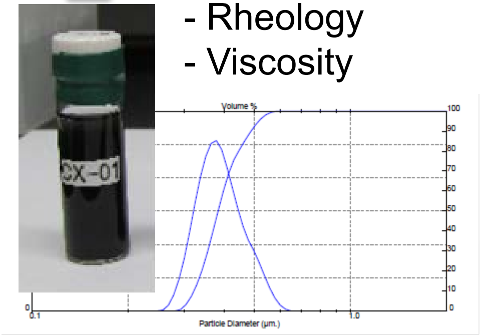
$$\begin{cases} \boldsymbol{i_V} & \geq \ 300 \text{ A/cm}^3 \ (iR\text{-free, } 80^\circ\text{C}) \\ \boldsymbol{P_{max}} & \geq \ 1.0 \text{ W/cm}^2 \ (80^\circ\text{C}) \\ \boldsymbol{\Delta E} & \leq \ 30 \text{ mV at } 0.8 \text{ A/cm}^2 \text{ after } 30.000 \text{ cycles} \end{cases}$$

Raw Materials | **Ink** | **Coating** | **Final MEA**

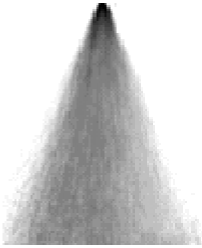




- Catalyst
- Membrane
- GDL



- Stability
- Rheology
- Viscosity



Substrate

- Electrode deposition

- CCM's
- 5 & 7-layer MEAs

- **Integrated custom ink delivery system**
- **Fine controllable CCM spray process**
- **Scalable MEA process**

- **Seven organizations with highly complementary skills and capabilities in catalyst development, electrode structure design, materials characterization, MEA fabrication, fuel cell system development and commercialization:**
  - ✓ Los Alamos National Laboratory and Oak Ridge National Laboratory – *direct DOE-EERE contracts*
  - ✓ Carnegie Mellon University, University of Rochester, University of Waterloo, General Motors, and IRD Fuel Cells – *subcontracts to Los Alamos National Laboratory*
- **Collaborations outside Fuel Cell Technologies Program (preliminary):**
  - ✓ *CellEra, Cesarea, Israel*
  - ✓ *Pajarito Powder, Albuquerque, New Mexico*
  - ✓ *Chevron Energy Technology Company, Richmond, California*

Proposed Future Work: Remainder of FY13 and FY14

Heat-Treated Catalysts and Alternative Supports:

- **Develop and optimize a multi-nitrogen-precursor heat-treated ORR catalysts with high volumetric activity and four-electron selectivity**
- **Synthesize non-PGM catalysts supported on highly-graphitic carbon(s) as a possible way of enhancing active-site density and improving durability**
- **Evaluate validity of metal-free approach in ORR electrocatalysis**

Non-Pyrolyzed Phthalocyanine-Derived Catalysts:

- **Synthesize and characterize Fe- and one Co-based phthalocyanine-derived catalysts with improved ORR activity ($E_{½} \geq 0.70$ V *vs.* RHE) and high four-electron selectivity; determine stability**
- **Initiate fuel cell testing of non-heat-treated ORR catalysts**

Performance Durability:

- **Develop durability and stress-test cycling protocols specific to non-PGM catalysts, (including a realistic potential/voltage window under specific environmental conditions of humidity, reagent stoichs, etc.)**
- **Optimize accelerated corrosion test to mimic decay mechanisms in long-term stack**
- **Propose activity/recovery cycles and evaluate their effectiveness**

Characterization:

- Validate surface-probe approach in identifying ORR active site(s)
- Implement advanced catalyst characterization methods (NRVS, MCD, Mößbauer, MES, low-voltage aberration-corrected STEM, high-resolution SEM/STEM, ICP, XRF, nano-XCT, X-ray absorption, TGA, porosimetry, etc.)

Active Site Determination:

- Validate surface-probe approach in non-PGM catalysis using one of well-performing early catalyst formulations

Electrode Design and Modeling:

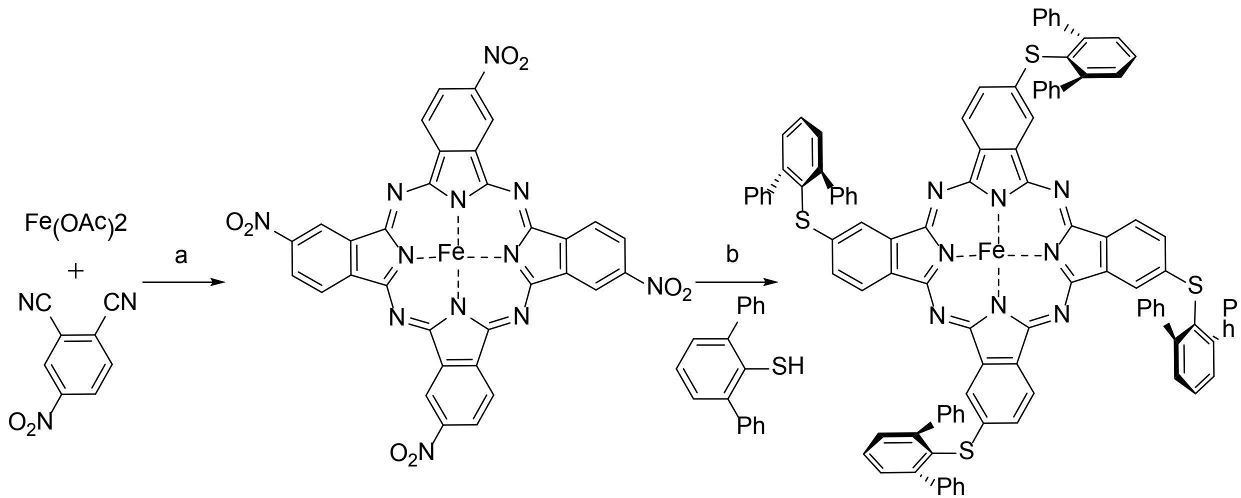
- Initiate predictive model for non-PGM catalyst layers (ORR activity, conductivity, and O_2 transport), based on knowledge acquired in earlier non-PGM studies at GM; perform preliminary model validation; refine model in conjunction with CMU's MES studies
- Adopt CMU's agglomerate model to non-PGM cathodes
- Complete implementation of the pore-scale model

MEA Fabrication and Optimization:

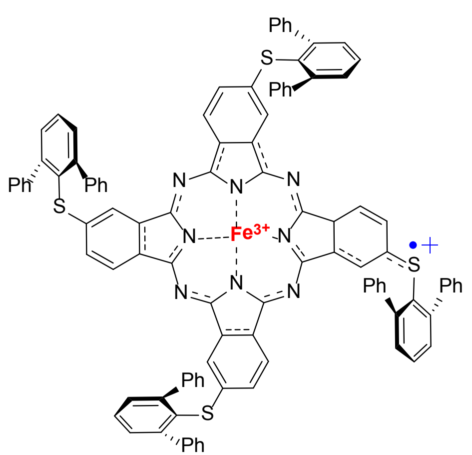
- Demonstrate Generation-1 spray-coated MEA with non-PGM cathode

Back-Up Slides

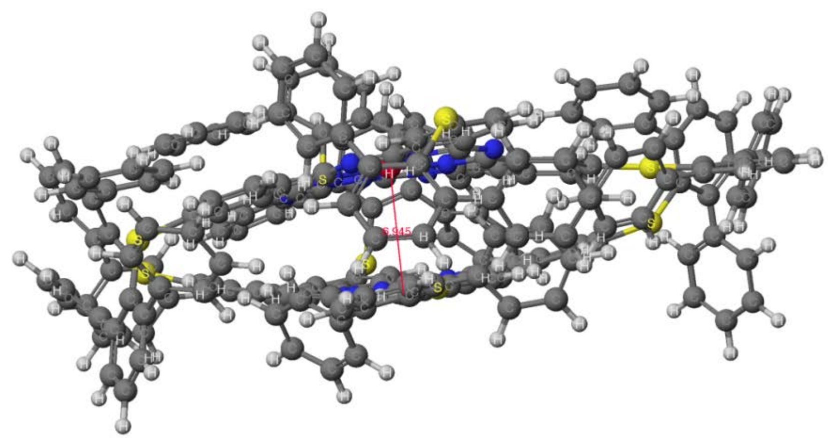
Catalyst Development: Synthesis of Phthalocyanine-Derived ORR Catalyst



Synthesis of Fe-SPc: (1) $Fe(OAc)_2$, quinoline, 210°C; (2) K_2CO_3, N-methylpyrrolidone, 180°C



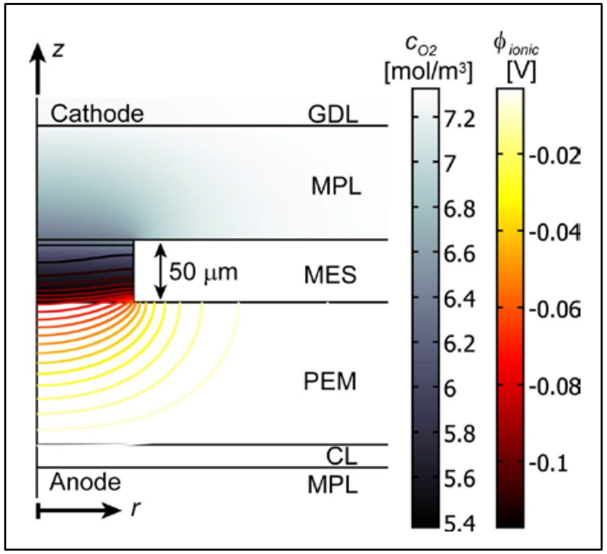
Providing electron storage sites



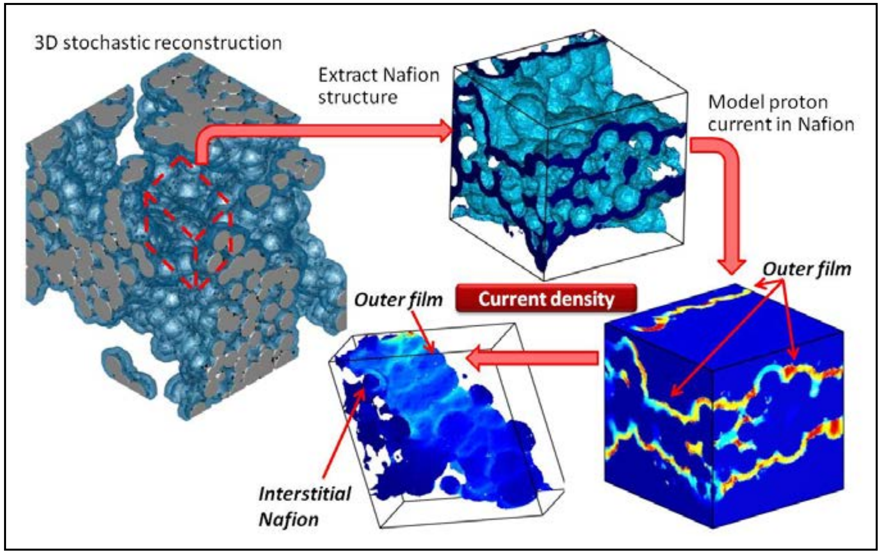
Stacking pattern of Fe-SPc (6.945 Å Fe-Fe distance) – possible active site configuration

Electrode Design: Computational Electrode Modeling

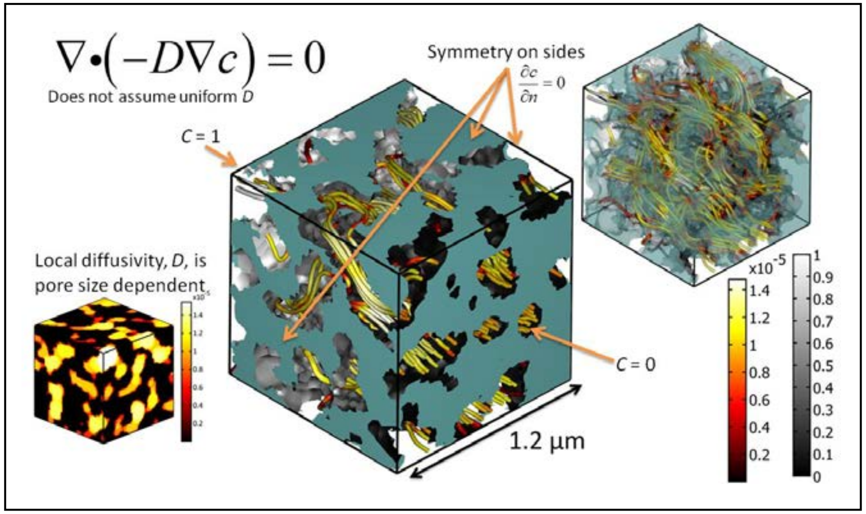
Macro-Modeling of Electrode and MEA

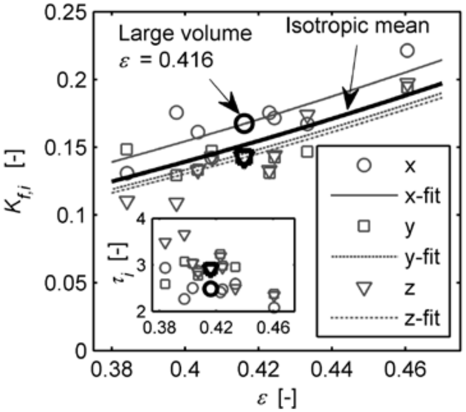


Particle-Scale Coupled Transport-Reaction Simulations



Effective Transport Properties from Transport Simulations on 3D Nano-XCT Geometry





Statistics for (i) porosity, (ii) formation factor, and (iii) tortuosity heterogeneity and anisotropy

Acknowledgments

- DOE-EERE Fuel Cell Technologies Office
- Technology Development Manager: Dr. Nancy Garland